

# Reinterpretation of Scanning Tunneling Microscopy on an Adsorbed Magnetic Atom

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(Dated: November 25, 2009)

The observation of the Kondo effect in mesoscopic systems under bias<sup>1,2</sup> has opened a new chapter in the physics of the Kondo phenomenon. Various types of  $dI/dV$ , where  $I$  and  $V$  denote current and source-drain (s-d) bias, respectively, line shapes have been measured by scanning tunneling microscopy (STM)<sup>1,3–11</sup>. However, explanation by single Fano line shape<sup>1,12–16</sup> is not relevant and even misleading. Here, we provide consistent explanations for various asymmetric and symmetric line shapes in terms of a microscopic theory that shows the creation of two resonant tunneling levels (RTLs) when bias is applied<sup>17</sup>. One side Kondo coupling between adatom and substrate does not create Kondo peak that appears only when the system has an overall Kondo coupling including both substrate and tip. The structure of an asymmetric line shape is mostly governed by the RTL peaks. Therefore, Kondo effect is negligible in most asymmetric line shapes.

The  $dI/dV$  line shapes measured by STM<sup>1,3–12</sup> can be classified into four different groups. Typical examples of such groups are given as follows: (i) a Co adatom on a Au(111)<sup>1</sup> or Cu(111)<sup>4–7</sup> surface showing a dip near zero bias; (ii) a Co adatom on a Cu(100) surface showing a significantly asymmetric line shape<sup>7,8</sup>; (iii) a Co adatom on an insulating Cu<sub>2</sub>N film covering a Cu(100) surface showing a sharp Kondo peak with symmetric shoulders<sup>9,10</sup>; and (iv) a system similar to (iii) with an Fe adatom showing a peculiar wedge and symmetric step-wise line shape<sup>11</sup>.

Since the existence of two RTLs is the new discovery of this study and plays a crucial role in explaining the line shape, we discuss it first. The occurrence of two RTLs is a unique characteristic of nonequilibrium steady state of a mesoscopic system with two reservoirs. Because of the back and forth transits between the Kondo impurity and the left and right reservoirs, two more basis vectors are needed to describe the dynamics of the system under bias compared with the system of single reservoir. These two additional basis vectors yield two RTLs. In equilibrium, however, these additional basis vectors are not needed because the probabilities of back and forth transits are the same. Only relevant nonequilibrium theories that can properly handle the Kondo phenomena in a steady state can verify the existence of the two RTLs. This resonant

tunneling is another type of coherent transport channel in addition to the Kondo channel. Interference between these two coherent scattering channels could yield Fano resonances<sup>18</sup> at the positions of the RTL because the RTLs are discrete states created within the continuum spectrum of the Kondo peak. However, only dispersed RTL peaks are observed in most STM line shapes instead of the sharp Fano interference pattern because no Kondo peak occurs except case (iii) mentioned above.

We employ Tersoff-Hamann formula<sup>19</sup> that gives the differential conductance of an STM system as

$$\frac{dI}{dV} \propto \Gamma^t \sum_{\sigma} \rho_{\sigma}^a(V),$$

where  $\Gamma^t$  denotes the featureless coupling function between adatom and STM tip, and  $\rho_{\sigma}^a(V)$  is the local density of states (LDOS) of the adatom at a steady state of bias  $V$ . The spectral function of an up-spin electron at the adatom is given by  $\rho_{\uparrow}^a(\omega) = (1/\pi)\text{Re}[(\mathbf{M}_r^{-1})_{33}]$ , where

$$\mathbf{M}_r = \begin{pmatrix} -i\tilde{\omega} & -\gamma_{ss} & U_{J-}^s & \gamma_{st} & \gamma_{J-} \\ \gamma_{ss} & -i\tilde{\omega} & U_{J+}^s & \gamma_{J+} & \gamma_{st} \\ -U_{J-}^{s*} & -U_{J+}^{s*} & -i\tilde{\omega} & -U_{J+}^{t*} & -U_{J-}^{t*} \\ -\gamma_{st} & -\gamma_{J+} & U_{J+}^t & -i\tilde{\omega} & \gamma_{tt} \\ -\gamma_{J-} & -\gamma_{st} & U_{J-}^t & -\gamma_{tt} & -i\tilde{\omega} \end{pmatrix},$$

where  $\omega' \equiv \omega - \epsilon_a - U\langle n_{a\downarrow} \rangle$ <sup>18</sup>. All the matrix elements, except the 8  $U$ -elements, have additional self-energy terms,  $\beta_{mn}[i\Sigma_0^s(\omega) + i\Sigma_0^t(\omega)] = 2\beta_{mn}\Delta$ , for a flat wide band, where  $\Delta \equiv (\Gamma^s + \Gamma^t)/4$ . We use  $\Delta$  to indicate the unit of energy.

We calculate the matrix elements of  $\mathbf{M}_r$  for the single-impurity Anderson model with two metallic reservoirs whose Hamiltonian is given by

$$\mathcal{H} = \sum_{k,\sigma,\alpha \in s,t} \epsilon_k c_{k\sigma}^{\alpha\dagger} c_{k\sigma}^{\alpha} + \sum_{\sigma} \epsilon_a c_{a\sigma}^{\dagger} c_{a\sigma} + U n_{a\uparrow} n_{a\downarrow} \\ + \sum_{k,\sigma,\alpha \in s,t} (V_{ka}^{\alpha} c_{a\sigma}^{\alpha\dagger} c_{k\sigma}^{\alpha} + V_{ka}^{\alpha*} c_{k\sigma}^{\alpha\dagger} c_{a\sigma}^{\alpha}),$$

where  $s, t, \epsilon_a$ , and  $U$  denote the substrate, tip, energy level of the adatom, and Coulomb interaction, respectively. The detailed procedure to reach the matrix  $\mathbf{M}_r$  and its elements is given in Supplementary information of this paper.

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The matrix  $\mathbf{M}_r$  contains all the information on the transport properties of the STM-Kondo systems. We discuss the roles of  $\gamma$  first and those of  $U_{J\pm}^{s,t}$  and the coefficients  $\beta_{mn}$  later. The upper-left  $3 \times 3$  block describes the single-reservoir Anderson model between the substrate and the magnetic adatom, while the lower-right  $3 \times 3$  block represents another single-reservoir Anderson model between the tip and the adatom. The  $2 \times 2$  blocks at the upper-right and lower-left corners couple the substrate and the tip through the adatom. Therefore,  $\gamma_{ss}(\gamma_{tt})$  represents the strength of the one-side Kondo coupling between the substrate (tip) and the adatom, and  $\gamma_{st}$  represents the coupling mechanism between the two reservoirs. On the other hand, the antidiagonal element  $\gamma_J$ , where  $\gamma_{J-} = \gamma_{J+} \equiv \gamma_J$ , gives the effect of steady state.

The operators comprising  $\gamma$ , which are given in Supplementary information of this paper, give clearer interpretations for the role of each  $\gamma$ . We present pictorial descriptions of  $\gamma$  in Fig. 1. Figure 1a shows the one-sided Kondo coupling of  $\gamma_{ss}(tt)$ ; Fig. 1b shows the difference between the leftward and rightward motions of a down-spin electron in  $\gamma_J$ ; Fig. 1c shows the overall Kondo coupling of  $\gamma_{st}$ , i.e., an up-spin electron in both reservoirs has Kondo coupling with a down-spin electron passing through the adatom via exchanging or hopping together. Figures 1b and 1c also show the resonant tunneling of a down-spin electron if it does not make a Kondo coupling with an up-spin electron.

In most of STM systems, no Kondo coupling exists between the adatom and tip, i.e.,  $\gamma_{tt} = 0$ . In this case, the system does not have an overall Kondo coupling and  $\gamma_{st} = \gamma_J$ . This implies that only resonant tunneling is allowed in Figs 1b and c. However, when the system has the overall Kondo coupling,  $\gamma_{st} > \gamma_J$  and both  $\gamma_{ss}$  and  $\gamma_{tt}$  are nonvanishing. In fact, the values of  $\gamma_{st}$  and  $\gamma_J$  at a steady state cannot be determined by present theory. However, we find that choosing appropriate constants for  $\gamma_{st}$  and  $\gamma_J$  gives rise to the  $dI/dV$  line shapes that are well-agreed with experiments.

Another important information is obtained from the matrix  $\mathbf{M}_r$ . The zeros of the determinant of  $\mathbf{M}_r$  in the atomic limit, i.e.,  $\Delta = 0$ , gives us the positions of five

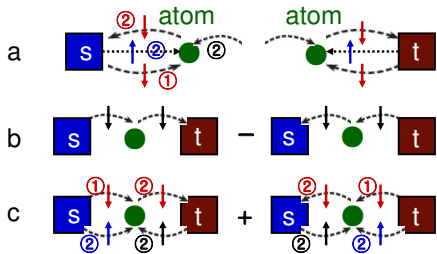


FIG. 1: Motions of a down-spin electron that makes a Kondo coupling with an up-spin electron. The processes indicated by number two are those of exchanging and hopping together. **a**,  $\gamma_{ss}$  and  $\gamma_{tt}$ , **b**,  $\gamma_J$ , and **c**,  $\gamma_{st}$ . We do not show up-spin movements in **b**. **b** and **c** also show the resonant tunneling of a down-spin when Kondo coupling is not constructed.

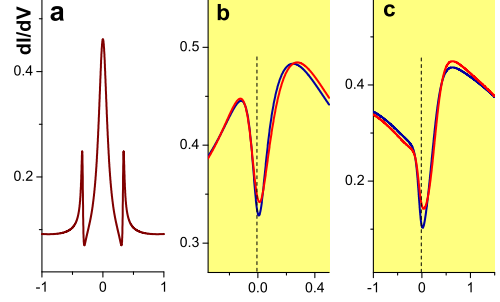


FIG. 2: Change in  $dI/dV$  line shape. The unit of the ordinate is  $(4e^2/h)\Gamma^t$ . We set  $U = 8$ . The unspecified parameters are the same as those used in the previous panel. **a**,  $\beta_{11} = 0.252$ ,  $\beta_{12} = 0.246$ ,  $\beta_{22} = 0.256$ , and other  $\beta_{mn} = 0.25$ .  $\gamma_{ss} = 0.12$ ,  $\gamma_{tt} = 0.1$ ,  $\gamma_{st} = 0.65$ ,  $\gamma_J = 0.35$ ,  $\text{Re}[U_{J+}^s] = 2.4$ , other  $\text{Re}[U_J] = 2$ , and  $\text{Im}[U_{J+}^{s,t}] = 0$ . **b**,  $\beta_{11} = 0.255$ ,  $\beta_{12} = 0.24$ ,  $\beta_{22} = 0.27$ ,  $\gamma_{tt} = 0$ ,  $\gamma_{st} = \gamma_J = 0.5$ ,  $\text{Re}[U_{J+}^{s,t}] = 0.5$ , and  $\text{Im}[U_{J+}^s] = 0.3$ . Dashed line:  $\gamma_{ss} = 0$ . **c**,  $\gamma_{st} = \gamma_J = 0.35$  and  $\text{Im}[U_{J+}^s] = 0.8$ .

peaks of the spectral function at the adatom. The five peaks are the Kondo peak at  $\omega' = 0$ , two Hubbard peaks at  $\omega' \approx \pm U/2$ , and two RTL peaks at  $\omega' = \pm[(\gamma_{ss}^2 + \gamma_{tt}^2)/2 + (\gamma_{st} - \gamma_J)^2 + O(U^{-2})]^{1/2}$ . The spectral weight of the Kondo peak can also be obtained from  $\mathbf{M}_r$  as

$$Z_{2R} = \left[ 1 + \frac{U^2 \{ \gamma_{ss}^2 + \gamma_{tt}^2 + 2(\gamma_{st} - \gamma_J)^2 \}}{8(\gamma_{ss}\gamma_{tt} + \gamma_{st}^2 - \gamma_J^2)^2} \right]^{-1}, \quad (1)$$

where the subscript  $2R$  indicates a two-reservoir system. It is interesting to note that when  $\gamma_{st} = \gamma_J$  and  $\gamma_{tt} = 0$ , which is the case of most STM-Kondo systems,  $Z_{2R}$  vanishes and the gap between the two RTLs is  $\sqrt{2}\gamma_{ss}$ . Since no Kondo peak exists in this case, the Kondo effect only appears as a separation of RTL peaks. One can see this case in the experiments on Co atom adsorbed on Au(111)<sup>1</sup> or Cu(111)<sup>4-7</sup> surface. On the other hand, when  $\gamma_{st} > \gamma_J$ , i.e.,  $\gamma_{tt} \neq 0$ ,  $Z_{2R}$  does not vanish and the gap between two RTLs becomes wider. This implies that the two RTLs recede by level repulsion due to the Kondo peak at the Fermi level. One can see this case in the experiments on Co atom adsorbed on Cu(100) surface covering with  $\text{Cu}_2\text{N}$ <sup>9-10</sup>.

We now show our theoretical  $dI/dV$  line shapes explicitly. Figure 2a, which is obtained by choosing  $\gamma_{ss} > \gamma_{tt} > 0$ ,  $\gamma_{st} > \gamma_J$ , and  $\text{Im}[U_{J+}^s] = 0$ , clearly shows both the Kondo and Fano peaks. However, the Kondo and Fano peaks disappear and only the RTL peaks remains as shown in Fig. 2b if we choose  $\gamma_{tt} = 0$ ,  $\gamma_{st} = \gamma_J$ , and  $\text{Im}[U_{J+}^s] > 0$ , which are the usual case of STM-Kondo system. Figure 2c is obtained by using a larger asymmetry parameter  $\text{Im}[U_{J+}^s]$ . The red lines in Figs. 2b and 2c correspond to the  $dI/dV$  line shapes observed in a Co adatom on a Cu(111)<sup>4</sup> and a Au(111)<sup>1</sup> substrate, respectively. A small shift in the dip from zero bias stems from the nonvanishing asymmetry parameter. The conditions  $\gamma_{st} = \gamma_J$  and  $\gamma_{tt} = 0$  eliminate the Kondo peak

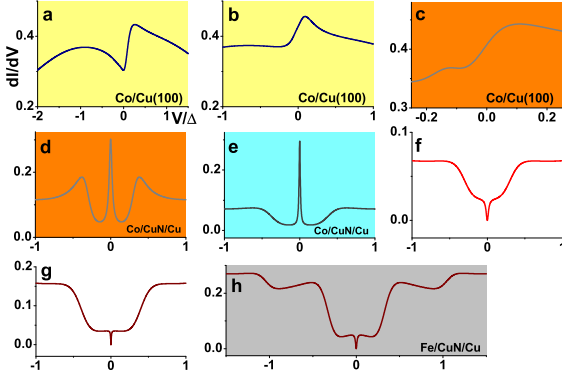


FIG. 3: Various  $dI/dV$  line shapes for  $U = 8$ . The unit of the ordinate and the presentation scheme are the same as Fig. 2. **a**,  $\beta_{11} = 0.265$ ,  $\beta_{12} = 0.23$ ,  $\beta_{22} = 0.28$ , and other  $\beta_{mn} = 1/4$ .  $\gamma_{ss} = \gamma_{tt} = 0$ , and  $\gamma_{st} = \gamma_J = 0.25$ .  $\text{Re}[U_{J\mp}^{s,t}] = 0.5$ ,  $\text{Im}[U_{J+}^s] = 0.4$ , and other  $\text{Im}[U_{J\mp}] = 0$ . **b**,  $\text{Im}[U_{J+}^s] = 0.2$ . **c**,  $\gamma_{ss} = 0.07$  and  $\text{Im}[U_{J+}^s] = 0.3$ . **d**,  $\beta_{11} = 0.251$ ,  $\beta_{12} = 0.249$  and  $\beta_{22} = 0.252$ .  $\gamma_{ss} = 0.3$ ,  $\gamma_{tt} = 0.1$ ,  $\gamma_{st} = 0.5$ , and  $\gamma_J = 0.4$ .  $\text{Re}[U_{J+}^s] = 2.4$ ,  $\text{Re}[U_{J+}^t] = 0.8$ , and  $\text{Im}[U_{J\mp}^{s,t}] = 0$ . **e**,  $\text{Re}[U_{J+}^s] = 4$ . **f**,  $\gamma_{tt} = 0$ ,  $\gamma_{st} = 0.4$ . **g**,  $\text{Re}[U_{J-}^{s,t}] = 0.8$ ,  $\text{Re}[U_{J+}^s] = 2.66$ , and  $\text{Re}[U_{J+}^t] = 1.33$ . **h**,  $\gamma_{ss} = 0.5$ ,  $\gamma_{st} = \gamma_J = 0.7$ ,  $\text{Re}[U_{J-}^{s,t}] = 0.4$ ,  $\text{Re}[U_{J+}^s] = 2$ , and  $\text{Re}[U_{J+}^t] = 1$ . Fermi level is shifted 0.1 to the right only in **c**. In **h**, two additional parameters have been used to take the spin excitation into account.

in Fig. 2a according to equation (1) and also changes the Fano resonance into a dispersed RTL peak because the Kondo spectrum, which is necessary for constructing Fano interference, has been removed.

The blue lines in Figs. 2b and c indicate the line shapes without the Kondo coupling in both sides, i.e.,  $\gamma_{ss} = \gamma_{tt} = 0$ . The similarity between the red and blue lines indicates that the structure of the  $dI/dV$  line shape is mostly governed by the RTL spectrum. The Kondo effect between a Co adatom and a substrate appears as a slight widening of the dip structure and a shift in the minimum. The amount of widening may be considered as an energy scale of the STM-Kondo system with dip structure because no Kondo peak appears in this case. We measure the increase  $\delta D$  in Fig. 2b, i.e., the difference between the gaps in red and blue, as  $\delta D = 0.1D$ , where  $D$  is the full distance of the gap in red. Since  $D$  in ref. 4 is approximately 20 meV, we obtain  $\delta D \approx 2.0$  meV for the system used by Manoharan *et al.*<sup>4</sup>. This energy corresponds to a temperature of 23 K that is considerably higher than the temperature at which usual STM measurements are performed. In order to measure the elongated gap, one must have a scheme to remove the Kondo coupling between the adatom and substrate.

Highly asymmetric line shapes have been observed in a Co adatom on a Cu(100) surface<sup>7-9</sup>. We obtain similar line shapes observed by Néel *et al.*<sup>8</sup> in Fig. 3a and b by adopting  $\gamma_{ss} = \gamma_{tt} = 0$ , which means that no Kondo effect is involved in obtaining these line shapes. However, a weak Kondo coupling between adatom and substrate is

needed to obtain Fig. 3c, which is the line shape reported by Choi, *et al.*<sup>9</sup> for the same system. In conclusion, no substantial Kondo coherence exists in the system of a Co adatom on a Cu(100) surface<sup>7-9</sup> that shows highly asymmetric  $dI/dV$  line shapes.

A remarkable change in the line shape occurs when the Cu(100) substrate is covered by an insulating copper nitride film. The line shape becomes symmetric, and a Kondo peak and side peaks<sup>9</sup> or steps<sup>10</sup> appear for a Co adatom. However, a peculiar wedge at zero bias and multiple steps appear for an Fe adatom<sup>11</sup>. Covering the Cu(100) surface with an insulating copper nitride film causes at least two effects. One is to strengthen the coherence in axial direction connecting Cu in substrate, Cu in film, and Co adatom. The other is to suppress both fluctuation  $\langle(\delta j_{a\downarrow}^{+s})^2\rangle^{1/2}$  and activity  $\langle j_{a\downarrow}^{+s}\rangle$  on the substrate side. The former results in the Kondo coupling between the adatom and tip and the latter makes  $\gamma_{ss}$  and  $\text{Re}[U_{J+}^s]$  increase. The latter also causes a decrease in  $\langle(\delta j_{a\downarrow}^{+t})^2\rangle^{1/2}$ . As a result, all the imaginary parts of  $U_{J\mp}^{s,t}$  vanish, and the line shape becomes symmetric.

On the basis of this analysis, we obtain a symmetric line shape with the Kondo peak and two RTL peaks as shown in Fig. 3d. This line shape corresponds to the one reported by Choi *et al.*<sup>9</sup>. Selecting a relatively large  $\text{Re}[U_{J+}^s]$  changes the RTL peaks of Fig. 3d to shoulders, as shown in Fig. 3e, which has been reported by Otte *et al.*<sup>10</sup>. An interesting change occurs when we simply choose  $\gamma_{st} = \gamma_J$  and  $\gamma_{tt} = 0$  in Fig. 3e to remove the Kondo peak. A sharp wedge appears at zero bias as shown in Fig. 3f. The wedge reflects the trace of a missing Kondo peak. Such a wedge has been observed by Hirjibehedin *et al.*<sup>11</sup> by adopting Fe adatom instead of Co. We show in Fig. 3g that a step-like feature can be obtained by changing  $\text{Re}[U_{J\pm}^{s,t}]$ . An additional step appears in the line shape of ref. 11. We understand that it stems from the spin-spin interaction at the position of the adatom. If we add the spin interaction at the adatom, the matrix  $\mathbf{M}_r$  becomes a  $7 \times 7$  matrix and additional steps appear as shown in Fig. 3h.

In conclusion, we have shown that two RTLs can explain most of the experiments on STM-Kondo systems consistently. If the Kondo coherence exists only in between a magnetic adatom and a substrate, the Kondo peak is not observed. The energy scale of the Kondo coherence in this case may be defined by the amount of gap elongation of the dip. Interestingly, the highly asymmetric line shapes are simply the RTL spectra with asymmetry. We showed that the Kondo peak and steps appearing in ref. 10 are attributed to the overall Kondo coupling and the suppression of the fluctuation on the substrate side. Finally, we understand that the sharp wedge for an Fe adatom reflects the trace of disappeared Kondo peak and the additional step stems from the spin interaction at the adsorbed atom.

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**Acknowledgements** This work was supported by the Korea Research Foundation, Grant No. KRF-2008-314-C00140.

**Supplementary Information:**  
**The Procedure Reaching Matrix  $\mathbf{M}_r$  and the Expressions of  $\beta_{mn}$**

The spectral function of a magnetic atom adsorbed on a substrate is given by  $\rho_{a\uparrow}(\omega) = -(1/\pi)\text{Im}G_{aa\uparrow}^+(\omega)$ . We show below that the spectral function  $\rho_{a\uparrow}(\omega)$  or the retarded Green's function  $G_{aa\uparrow}^+(\omega)$  can be expressed by the matrix  $\mathbf{M}_r^{-1}$  given in the text of the main article. Since the retarded Green's function expressed in a resolvent form in the Heisenberg picture is written as<sup>1</sup>

$$iG_{aa\uparrow}^+(z) = \langle c_{a\uparrow} | (z\mathbf{I} + i\mathbf{L})^{-1} | c_{a\uparrow} \rangle = (\mathbf{M}^{-1})_{aa},$$

where  $\mathbf{L}$  is the Liouville operator defined by  $\mathbf{L}\hat{\mathcal{O}} = [\mathcal{H}, \hat{\mathcal{O}}]$  for the Hamiltonian  $\mathcal{H}$ ,  $z = -i\omega + 0^+$ ,  $c_{a\uparrow}$  indicates the annihilation of an up-spin electron at the adsorbed atom, and the matrix  $\mathbf{M}$  is constructed by the elements  $\mathbf{M}_{k\ell} = z\delta_{k\ell} + \langle e_\ell | i\mathbf{L} e_k \rangle$ , where the vectors  $e_\ell$  and  $e_k$  are the elements of a complete set of orthonormal basis vectors  $\{e_\ell | \ell = 1, \dots, \infty\}$  spanning the Liouville space. The operator  $c_{a\uparrow}$  is one of the members. The inner product is defined by  $\langle e_k | e_\ell \rangle \equiv \langle \{e_k, e_\ell^\dagger\} \rangle$ , where the angular and curly brackets denote the expectation value and anticommutator, respectively.

Therefore, the first step to obtain the retarded Green's function  $G_{aa\uparrow}^+(\omega)$  is to find a complete set of orthonormal basis vectors of the Liouville space. In ref. 2 given below, we have shown a basis spanning the reduced Liouville space that is effective for describing the dynamics of the system in the Kondo regime as

$$(c_{k\uparrow}^s, \quad \delta n_{a\downarrow} c_{k\uparrow}^s, \quad \delta j_{a\downarrow}^{+s} c_{a\uparrow}, \quad \delta j_{a\downarrow}^{-s} c_{a\uparrow}, \quad c_{a\uparrow}, \quad \delta j_{a\downarrow}^{-t} c_{a\uparrow}, \quad \delta j_{a\downarrow}^{+t} c_{a\uparrow}, \quad \delta n_{a\downarrow} c_{k\uparrow}^t, \quad c_{k\uparrow}^t)$$

with normalization factors  $\langle (\delta n_{a\downarrow})^2 \rangle^{-1/2}$  and  $\langle (\delta j_{a\downarrow}^{\mp s,t})^2 \rangle^{-1/2}$  for the corresponding basis vectors, where  $\delta\mathcal{O} = \mathcal{O} - \langle \mathcal{O} \rangle$ ,  $j_{a\downarrow}^{\mp s,t} = (i) \sum_k (V_{ka}^{s,t} c_{a\downarrow}^\dagger c_{k\downarrow}^{s,t} \mp V_{ka}^{*s,t} c_{k\downarrow}^{\dagger s,t} c_{a\downarrow})$ , where  $(i)$  is deleted for  $j_{a\downarrow}^{+s,t}$ , and  $k = 1, 2, \dots, \infty$  indicates the quantum states of the substrate or the tip.

We construct the full matrix  $\mathbf{M}$  using these basis vectors in an order given above. Then,  $\mathbf{M}$  is given by the following nine-block matrix,

$$\mathbf{M} = \begin{pmatrix} \mathbf{M}_{ss} & \mathbf{M}_{as} & \mathbf{0} \\ \mathbf{M}_{sa} & \mathbf{M}_a & \mathbf{M}_{ta} \\ \mathbf{0} & \mathbf{M}_{at} & \mathbf{M}_{tt} \end{pmatrix}, \quad (S1)$$

where the blocks  $\mathbf{M}_a$ ,  $\mathbf{M}_{as}$  and  $\mathbf{M}_{at}$ , and  $\mathbf{M}_{sa}$  and  $\mathbf{M}_{ta}$  are  $5 \times 5$ ,  $5 \times \infty$ , and  $\infty \times 5$  matrices, respectively. Since no direct coupling exists between the substrate and tip, null blocks occur at the two corners. The block  $\mathbf{M}_{ss(tt)}$  is constructed by the basis vectors  $c_{k\uparrow}^{s(t)}$  and  $\delta n_{a\downarrow} c_{k\uparrow}^{s(t)}$ . It is written as

$$\mathbf{M}_{ss(tt)} = \begin{bmatrix} \mathbf{M}_{11} & \mathbf{0} \\ \mathbf{0} & \mathbf{M}_{11} \end{bmatrix},$$

where

$$\mathbf{M}_{11} = \begin{pmatrix} z + i\epsilon_1 & 0 & \cdots & 0 \\ 0 & \ddots & & 0 \\ 0 & \cdots & 0 & z + i\epsilon_\infty \end{pmatrix}.$$

On the other hand,  $\mathbf{M}_{sa} = -\mathbf{M}_{as}^\dagger$  and the  $5 \times \infty$  block  $\mathbf{M}_{as}$  has the form

$$\mathbf{M}_{as} = \begin{bmatrix} \mathbf{0} & \mathbf{0} & \mathbf{C}_{ka} & \mathbf{0} & \mathbf{0} \\ \mathbf{C}_{nj-}^s & \mathbf{C}_{nj+}^s & \mathbf{0} & \mathbf{C}_{nj+}^t & \mathbf{C}_{nj-}^t \end{bmatrix},$$

where the columns  $\mathbf{C}_{ka}$ ,  $\mathbf{C}_{nj-}^{s,t}$ , and  $\mathbf{C}_{nj+}^{s,t}$  have elements  $iV_{ka}^*$ ,  $-(\xi_a^{-s,t} V_{ka})^*$ , and  $-(\xi_a^{+s,t} V_{ka})^*$ , respectively, where

$$\xi_a^{\mp s,t} = (1/2)[\langle i[n_{a\downarrow}, j_{a\downarrow}^{\mp s,t}] (1 - 2n_{a\uparrow}) \rangle + i(1 - 2\langle n_{a\downarrow} \rangle) \langle j_{a\downarrow}^{\mp s,t} \rangle] [\langle (\delta j_{a\downarrow}^{\mp s,t})^2 \rangle \langle (\delta n_{a\downarrow})^2 \rangle]^{-1/2}.$$

The first term is purely real and the second term is purely imaginary. The detailed process of obtaining  $\xi_a^{\mp s, t} V_{ka}$  from  $-\langle i\mathbf{L}c_{k\uparrow}\delta n_{a\downarrow}|c_{a\uparrow}\delta j_{a\downarrow}^{\mp}\rangle$ , which is the element of  $\mathbf{M}_{sa}$ , is given in Appendix A below.

The  $5 \times 5$  block  $\mathbf{M}_a$  at center is given by

$$\mathbf{M}_a = \begin{pmatrix} -i\tilde{\omega} & -\gamma_{ss} & U_{J-}^s & \gamma_{st} & \gamma_{J-} \\ \gamma_{ss} & -i\tilde{\omega} & U_{J+}^s & \gamma_{J+} & \gamma_{st} \\ -U_{J-}^{s*} & -U_{J+}^{s*} & -i\tilde{\omega} & -U_{J+}^{t*} & -U_{J-}^{t*} \\ -\gamma_{st} & -\gamma_{J+} & U_{J+}^t & -i\tilde{\omega} & \gamma_{tt} \\ -\gamma_{J-} & -\gamma_{st} & U_{J-}^t & -\gamma_{tt} & -i\tilde{\omega} \end{pmatrix},$$

where  $\tilde{\omega} \equiv \omega - \epsilon_a - U\langle n_{a\downarrow} \rangle$ .  $\gamma$  and  $U_{J\mp}^{s,t}$  are given by

$$\gamma_{ss}(tt) = \langle \sum_k i(V_{ka}^* c_{k\uparrow}^s + V_{ka}^* c_{k\uparrow}^t) c_{a\uparrow}^\dagger [j_{a\downarrow}^{-s(t)}, j_{a\downarrow}^{+s(t)}] [\langle (\delta j_{a\downarrow}^{-s(t)})^2 \rangle \langle (\delta j_{a\downarrow}^{+s(t)})^2 \rangle]^{-1/2},$$

$$\gamma_{st} = \langle \sum_k i(V_{ka}^* c_{k\uparrow}^s + V_{ka}^* c_{k\uparrow}^t) c_{a\uparrow}^\dagger [j_{a\downarrow}^{-s}, j_{a\downarrow}^{+t}] [\langle (\delta j_{a\downarrow}^{-s})^2 \rangle \langle (\delta j_{a\downarrow}^{+t})^2 \rangle]^{-1/2},$$

$$\gamma_{J\mp} = \langle \sum_k i(V_{ka}^* c_{k\uparrow}^s + V_{ka}^* c_{k\uparrow}^t) c_{a\uparrow}^\dagger [j_{a\downarrow}^{\mp s}, j_{a\downarrow}^{\mp t}] [\langle (\delta j_{a\downarrow}^{\mp s})^2 \rangle \langle (\delta j_{a\downarrow}^{\mp t})^2 \rangle]^{-1/2},$$

and

$$U_{J\mp}^{s,t} = \frac{iU}{2} \left[ \frac{\langle [n_{a\downarrow}, j_{a\downarrow}^{\mp s, t}] (1 - 2n_{a\uparrow}) \rangle + \langle j_{a\downarrow}^{\mp s, t} \rangle (1 - 2\langle n_{a\downarrow} \rangle)}{\langle (\delta j_{a\downarrow}^{\mp s, t})^2 \rangle^{1/2}} \right].$$

The detailed process of calculation of the matrix elements is given in Appendix A in which the Hamiltonian for the single reservoir Anderson model is used.

The infinite-dimensional matrix  $\mathbf{M}$  of equation (S1) can be reduced to an equivalent  $5 \times 5$ -dimensional matrix using Löwdin's partitioning technique<sup>3,4</sup>. For this purpose, we consider an eigenvalue equation  $\mathbf{M}\mathbf{C} = \mathbf{0}$ , where  $\mathbf{C}$  and  $\mathbf{0}$  are column vectors. We partition the column vector  $\mathbf{C}$  into three parts, i.e.,  $\mathbf{C} = (\mathbf{C}_s \mathbf{C}_a \mathbf{C}_t)^T$ , where  $T$  means the transpose and  $\mathbf{C}_s$ ,  $\mathbf{C}_a$ , and  $\mathbf{C}_t$  correspond to rows  $(c_{k\uparrow}^s, \delta n_{a\downarrow} c_{k\uparrow}^s)$ ,  $(\delta j_{a\downarrow}^{+s} c_{a\uparrow}, \delta j_{a\downarrow}^{-s} c_{a\uparrow}, c_{a\uparrow}, \delta j_{a\downarrow}^{-t} c_{a\uparrow}, \delta j_{a\downarrow}^{+t} c_{a\uparrow})$ , and  $(\delta n_{a\downarrow} c_{k\uparrow}^t, c_{k\uparrow}^t)$ , respectively. After eliminating  $\mathbf{C}_s$  and  $\mathbf{C}_t$ , we reach an equation  $(\mathbf{M}_a - \mathbf{M}_{sa} \mathbf{M}_{ss}^{-1} \mathbf{M}_{as} - \mathbf{M}_{ta} \mathbf{M}_{tt}^{-1} \mathbf{M}_{at}) \mathbf{C}_a \equiv \mathbf{M}_r \mathbf{C}_a = \mathbf{0}$ . Then, we have the expression of the reduced matrix  $\mathbf{M}_r$  given in the text, i.e.,

$$\mathbf{M}_r = \begin{pmatrix} -i\tilde{\omega} + i\Sigma_{11}(\omega) & -\gamma_{ss} + i\Sigma_{12}(\omega) & U_{J-}^s & \gamma_{st} + i\Sigma_{14}(\omega) & \gamma_{J-} + i\Sigma_{15}(\omega) \\ \gamma_{ss} + i\Sigma_{21}(\omega) & -i\tilde{\omega} + i\Sigma_{22}(\omega) & U_{J+}^s & \gamma_{J+} + i\Sigma_{24}(\omega) & \gamma_{st} + i\Sigma_{25}(\omega) \\ -U_{J-}^{s*} & -U_{J+}^{s*} & -i\tilde{\omega} + i\Sigma_{33}(\omega) & -U_{J-}^{t*} & -U_{J+}^{t*} \\ -\gamma_{st} + i\Sigma_{41}(\omega) & -\gamma_{J+} + i\Sigma_{42}(\omega) & U_{J+}^t & -i\tilde{\omega} + i\Sigma_{44}(\omega) & \gamma_{tt} + i\Sigma_{45}(\omega) \\ -\gamma_{J-} + i\Sigma_{51}(\omega) & -\gamma_{st} + i\Sigma_{52}(\omega) & U_{J-}^t & -\gamma_{tt} + i\Sigma_{54}(\omega) & -i\tilde{\omega} + i\Sigma_{55}(\omega) \end{pmatrix},$$

where  $i\Sigma_{mn}(\omega) = \beta_{mn}(i\Sigma_0^s(\omega) + i\Sigma_0^t(\omega)) = 2\beta_{mn}\Delta$  for a flat wide-band, where  $\Delta \equiv (\Delta^s + \Delta^t)/2 = (\Gamma^s + \Gamma^t)/4$ .  $\Delta$  is used as a unit of energy. The coefficients  $\beta_{mn}$  are symmetric. They are given by  $\beta_{11} = |\xi_a^{-s}|^2$ ,  $\beta_{22} = |\xi_a^{+s}|^2$ ,  $\beta_{33} = 1$ ,  $\beta_{44} = |\xi_a^{+t}|^2$ ,  $\beta_{55} = |\xi_a^{-t}|^2$ ,  $\beta_{24} = \xi_a^{+s*} \xi_a^{+t}$ ,  $\beta_{12} = \xi_a^{-s*} \xi_a^{+s}$ ,  $\beta_{14} = \xi_a^{-s*} \xi_a^{+t}$ ,  $\beta_{15} = \xi_a^{-s*} \xi_a^{-t}$ ,  $\beta_{25} = \xi_a^{+s*} \xi_a^{-t}$ , and  $\beta_{45} = \xi_a^{+t*} \xi_a^{-t}$ . The coefficients  $\beta_{mn}$  are complex when  $m \neq n$ , while  $\beta_{mm}$  are real. The detailed expressions of  $\beta_{mn}$  are given in Appendix B.

## Appendix A

Calculation of the matrix elements of  $\mathbf{M}$  for the single-impurity Anderson model with one reservoir is shown below. Since calculation for the elements of  $\mathbf{M}_{ss}(tt)$  is very simple, we skip it.

(1) Matrix elements of the block  $\mathbf{M}_{sa}$ :

$$\begin{aligned} & \text{Nontrivial elements of } \mathbf{M}_{sa} \text{ are } -\langle \{i\mathbf{L}(c_{k\uparrow}\delta n_{a\downarrow}), \delta j_{a\downarrow}^{\mp} c_{a\uparrow}^\dagger\} \rangle, \text{ i.e.,} \\ & \langle \{i[H, c_{k\uparrow}\delta n_{a\downarrow}], j_{a\downarrow}^{\mp} c_{a\uparrow}^\dagger\} \rangle = \langle \{i[H, c_{k\uparrow}]\delta n_{a\downarrow} + c_{k\uparrow}i[H, n_{a\downarrow}], \delta j_{a\downarrow}^{\mp} c_{a\uparrow}^\dagger\} \rangle \\ & = -i\epsilon_k \langle \{c_{k\uparrow}\delta n_{a\downarrow}, \delta j_{a\downarrow}^{\mp} c_{a\uparrow}^\dagger\} \rangle - iV_{ka} \langle \{c_{a\uparrow}\delta n_{a\downarrow}, \delta j_{a\downarrow}^{\mp} c_{a\uparrow}^\dagger\} \rangle + \langle \{c_{k\uparrow}j_{a\downarrow}^-, \delta j_{a\downarrow}^{\mp} c_{a\uparrow}^\dagger\} \rangle. \end{aligned} \quad \text{The first term}$$

$(-i\epsilon_k)\langle\{c_{k\uparrow}\delta n_{a\downarrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle = (-i\epsilon_k)\langle[n_{a\downarrow}, j_{a\downarrow}^\mp]c_{k\uparrow}c_{a\uparrow}^\dagger\rangle$  should vanish because the up-spin dynamics of this form is not allowed. The third term also vanishes because  $\langle\{c_{k\uparrow}j_{a\downarrow}^\mp, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle = \langle j_{a\downarrow}^\mp \delta j_{a\downarrow}^\mp \{c_{k\uparrow}, c_{a\uparrow}^\dagger\}\rangle = 0$ . The second term, however, must be calculated rigorously, since it is a hybridization term that is related to the Kondo process. The operator  $\{c_{a\uparrow}\delta n_{a\downarrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}$  is expanded as  $c_{a\uparrow}[\delta n_{a\downarrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger] + [\delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger, c_{a\uparrow}]\delta n_{a\downarrow} + 2c_{a\uparrow}\delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\delta n_{a\downarrow}$ . First two terms are rewritten as  $c_{a\uparrow}[\delta n_{a\downarrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger] = c_{a\uparrow}[n_{a\downarrow}, j_{a\downarrow}^\mp]c_{a\uparrow}^\dagger = c_{a\uparrow}c_{a\uparrow}^\dagger[n_{a\downarrow}, j_{a\downarrow}^\mp] = (1 - n_{a\uparrow})[n_{a\downarrow}, j_{a\downarrow}^\mp]$  and  $[\delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger, c_{a\uparrow}]\delta n_{a\downarrow} = \delta j_{a\downarrow}^\mp [c_{a\uparrow}^\dagger, c_{a\uparrow}]\delta n_{a\downarrow} = \delta j_{a\downarrow}^\mp (1 - 2c_{a\uparrow}c_{a\uparrow}^\dagger)\delta n_{a\downarrow}$ , while the third term is cancelled by the last expression  $-2c_{a\uparrow}\delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\delta n_{a\downarrow}$ . Hence,  $-\langle\{i\mathbf{L}(c_{k\uparrow}\delta n_{a\downarrow}), j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle = iV_{ka}\langle(1 - n_{a\uparrow})[n_{a\downarrow}, \delta j_{a\downarrow}^\mp] + \delta j_{a\downarrow}^\mp\delta n_{a\downarrow}\rangle = iV_{ka}\langle(\frac{1}{2} - n_{a\uparrow})[n_{a\downarrow}, j_{a\downarrow}^\mp] + \frac{1}{2}[n_{a\downarrow}, j_{a\downarrow}^\mp] + \delta j_{a\downarrow}^\mp\delta n_{a\downarrow}\rangle = \frac{iV_{ka}}{2}\langle(1 - 2n_{a\uparrow})[n_{a\downarrow}, j_{a\downarrow}^\mp] + \{\delta n_{a\downarrow}, \delta j_{a\downarrow}^\mp\}\rangle = \frac{iV_{ka}}{2}\langle(1 - 2n_{a\uparrow})[n_{a\downarrow}, j_{a\downarrow}^\mp] + (1 - 2\langle n_{a\downarrow}\rangle)\langle j_{a\downarrow}^\mp\rangle\rangle$ .

Therefore, the matrix elements  $-\frac{\langle\{i\mathbf{L}(c_{k\uparrow}\delta n_{a\downarrow}), \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle}{||c_{k\uparrow}\delta n_{a\downarrow}|| \times ||c_{a\uparrow}\delta j_{a\downarrow}^\mp||} = V_{ka}\xi_a^\mp$ , where  $\xi_a^\mp = \frac{1}{2}\{\langle i(1 - 2n_{a\uparrow})[n_{a\downarrow}, j_{a\downarrow}^\mp]\rangle + i(1 - 2\langle n_{a\downarrow}\rangle)\langle j_{a\downarrow}^\mp\rangle\}\langle(\delta n_{a\downarrow})^2\rangle^{-1/2}\langle(\delta j_{a\downarrow}^\mp)^2\rangle^{-1/2}$ .

## (2) Matrix elements of the block $\mathbf{M}_a$ :

### (2-1) Diagonal elements:

By using the commutator expression  $i[H, c_{a\uparrow}] = -i\sum_{\mathbf{k}} V_{\mathbf{k}a}^* c_{\mathbf{k}\uparrow} - i\epsilon_a c_{a\uparrow} - iU c_{a\uparrow} n_{a\downarrow}$ , the diagonal elements of the block  $\mathbf{M}_a$  are given by

$$(A) -\langle\{i[H, c_{a\uparrow}], c_{a\uparrow}^\dagger\}\rangle = i\sum_{\mathbf{k}} V_{\mathbf{k}a}^* \langle\{c_{\mathbf{k}\uparrow}, c_{a\uparrow}^\dagger\}\rangle + i\epsilon_a \langle\{c_{a\uparrow}, c_{a\uparrow}^\dagger\}\rangle + iU \langle\{c_{a\uparrow} n_{a\downarrow}, c_{a\uparrow}^\dagger\}\rangle$$

$$= i\epsilon_a + iU \langle\{c_{a\uparrow} n_{a\downarrow}, c_{a\uparrow}^\dagger\}\rangle = i\epsilon_a + iU \langle\{c_{a\uparrow}, c_{a\uparrow}^\dagger\} n_{a\downarrow}\rangle = i\epsilon_a + iU \langle n_{a\downarrow}\rangle, \text{ and}$$

(B)  $-\langle\{i[H, c_{a\uparrow} \delta j_{a\downarrow}^\mp], (c_{a\uparrow} \delta j_{a\downarrow}^\mp)^\dagger\}\rangle = -\langle\{i[H, c_{a\uparrow}] \delta j_{a\downarrow}^\mp, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle - \langle\{c_{a\uparrow} i[H, \delta j_{a\downarrow}^\mp], \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle$ . The first term of (B) is rewritten as

$$\langle\{i[H, c_{a\uparrow}] \delta j_{a\downarrow}^\mp, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle = \langle\{(-i\sum_{\mathbf{k}} V_{\mathbf{k}a}^* c_{\mathbf{k}\uparrow} - i\epsilon_a c_{a\uparrow} - iU c_{a\uparrow} n_{a\downarrow}) \delta j_{a\downarrow}^\mp, (c_{a\uparrow} \delta j_{a\downarrow}^\mp)^\dagger\}\rangle$$

$$= -i\epsilon_a \langle\{c_{a\uparrow} \delta j_{a\downarrow}^\mp, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle - iU \langle\{c_{a\uparrow} n_{a\downarrow} \delta j_{a\downarrow}^\mp, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle$$
. Applying the decoupling approximation,  $n_{a\downarrow} \delta j_{a\downarrow}^\mp = \langle n_{a\downarrow} \rangle \delta j_{a\downarrow}^\mp$ , to the  $U$ -term above gives rise to a form of squared norm for the first term of (B), i.e.,  $\langle\{i[H, c_{a\uparrow}] \delta j_{a\downarrow}^\mp, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle = [-i\epsilon_a - iU \langle n_{a\downarrow} \rangle] \times ||c_{a\uparrow} \delta j_{a\downarrow}^\mp||^2$ . The second term of (B), however, cannot be written in the form of a squared norm, because  $[H, j_{a\downarrow}^\mp] \propto j_{a\downarrow}^\pm$ . Therefore, we neglect it.

### (2-2) Matrix elements $U_{J\mp}$ :

These are given by the inner products  $-\langle\{i\mathbf{L}c_{a\uparrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle$ , i.e.,  $-\langle\{i[H, c_{a\uparrow}], \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle$

$$= i\epsilon_a \langle\delta j_{a\downarrow}^\mp\rangle \langle\{c_{a\uparrow}, c_{a\uparrow}^\dagger\}\rangle + iU \langle\{c_{a\uparrow} n_{a\downarrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle + i\sum_{\mathbf{k}} V_{\mathbf{k}a}^* \langle\delta j_{a\downarrow}^\mp\rangle \langle\{c_{\mathbf{k}\uparrow}, c_{a\uparrow}^\dagger\}\rangle$$

$$= iU \langle\{c_{a\uparrow} n_{a\downarrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle$$
. However,  $\langle\{c_{a\uparrow} \delta n_{a\downarrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle = \langle c_{a\uparrow} [\delta n_{a\downarrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger] \rangle$ 

$$+ \langle [\delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger, c_{a\uparrow}] \delta n_{a\downarrow} \rangle + \langle 2c_{a\uparrow} \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger \delta n_{a\downarrow} \rangle$$
, where the operator in the first term is rewritten as  $c_{a\uparrow} [\delta n_{a\downarrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger] = c_{a\uparrow} [n_{a\downarrow}, j_{a\downarrow}^\mp] c_{a\uparrow}^\dagger = c_{a\uparrow} c_{a\uparrow}^\dagger [n_{a\downarrow}, j_{a\downarrow}^\mp] = (1 - n_{a\uparrow}) [n_{a\downarrow}, j_{a\downarrow}^\mp]$ , while the second term is given by  $\langle [\delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger, c_{a\uparrow}] \delta n_{a\downarrow} \rangle = \langle \delta j_{a\downarrow}^\mp [c_{a\uparrow}^\dagger, c_{a\uparrow}] \delta n_{a\downarrow} \rangle = \langle \delta j_{a\downarrow}^\mp \delta n_{a\downarrow} \rangle - \langle 2\delta j_{a\downarrow}^\mp c_{a\uparrow} c_{a\uparrow}^\dagger \delta n_{a\downarrow} \rangle$ . The last one cancels the third term of  $\langle\{c_{a\uparrow} \delta n_{a\downarrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle$  above. Hence,  $\langle\{c_{a\uparrow} \delta n_{a\downarrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle$ 

$$= \langle(1 - n_{a\uparrow}) [n_{a\downarrow}, j_{a\downarrow}^\mp] + \delta j_{a\downarrow}^\mp \delta n_{a\downarrow}\rangle = \langle(\frac{1}{2} - n_{a\uparrow}) [n_{a\downarrow}, j_{a\downarrow}^\mp] + \frac{1}{2} [n_{a\downarrow}, \delta j_{a\downarrow}^\mp] + \delta j_{a\downarrow}^\mp \delta n_{a\downarrow}\rangle$$

$$= \frac{1}{2} \langle(1 - 2n_{a\uparrow}) [n_{a\downarrow}, j_{a\downarrow}^\mp] + \{\delta n_{a\downarrow}, \delta j_{a\downarrow}^\mp\}\rangle = \frac{1}{2} \{\langle(1 - 2n_{a\uparrow}) [n_{a\downarrow}, j_{a\downarrow}^\mp]\rangle + (1 - 2\langle n_{a\downarrow}\rangle) \langle j_{a\downarrow}^\mp \rangle\}$$
.

Therefore, the matrix elements  $U_{J\mp}$  that are defined by  $-\frac{\langle\{i\mathbf{L}c_{a\uparrow}, \delta j_{a\downarrow}^\mp c_{a\uparrow}^\dagger\}\rangle}{\langle(\delta j_{a\downarrow}^\mp)^2\rangle^{1/2}}$  are given by

$$U_{J\mp} = \frac{U}{2} [i\langle(1 - 2n_{a\uparrow}) [n_{a\downarrow}, j_{a\downarrow}^\mp]\rangle + i(1 - 2\langle n_{a\downarrow}\rangle) \langle j_{a\downarrow}^\mp \rangle] \langle(\delta j_{a\downarrow}^\mp)^2\rangle^{-1/2}$$

If we define  $\text{Re}[U_{J\mp}] \equiv U/2\tau$ , we get  $\tau = 2$  by the atomic limit analysis for the two-reservoir Anderson model<sup>5</sup>. Then, we have a relation,  $1/\tau = i\langle(1 - 2n_{a\uparrow}) [n_{a\downarrow}, j_{a\downarrow}^\mp]\rangle \langle(\delta j_{a\downarrow}^\mp)^2\rangle^{-1/2}$ , which will be used in Appendix B.

### (2-3) Matrix elements $\gamma_{ss(tt)}$ :

The inner products  $-\langle\{i\mathbf{L}(c_{a\uparrow} \delta j_{a\downarrow}^\mp), \delta j_{a\downarrow}^\pm c_{a\uparrow}^\dagger\}\rangle$  gives rise to the expressions for  $\gamma_{ss(tt)}$ . Since  $\langle\{i\mathbf{L}(c_{a\uparrow} \delta j_{a\downarrow}^\mp), \delta j_{a\downarrow}^\pm c_{a\uparrow}^\dagger\}\rangle = \langle\{i[H, c_{a\uparrow}] \delta j_{a\downarrow}^\mp, \delta j_{a\downarrow}^\pm c_{a\uparrow}^\dagger\}\rangle + \langle\{c_{a\uparrow} i[H, j_{a\downarrow}^\mp], \delta j_{a\downarrow}^\pm c_{a\uparrow}^\dagger\}\rangle$ , the first term can be expanded as  $\langle\{i[H, c_{a\uparrow}] \delta j_{a\downarrow}^\mp, \delta j_{a\downarrow}^\pm c_{a\uparrow}^\dagger\}\rangle = -i\epsilon_a \langle\{c_{a\uparrow} \delta j_{a\downarrow}^\mp, \delta j_{a\downarrow}^\pm c_{a\uparrow}^\dagger\}\rangle - iU \langle\{c_{a\uparrow} n_{a\downarrow} \delta j_{a\downarrow}^\mp, \delta j_{a\downarrow}^\pm c_{a\uparrow}^\dagger\}\rangle - i\sum_{\mathbf{k}} V_{\mathbf{k}a}^* \langle\{c_{\mathbf{k}\uparrow} \delta j_{a\downarrow}^\mp, \delta j_{a\downarrow}^\pm c_{a\uparrow}^\dagger\}\rangle$ .

The first and second terms of this expression should vanish because they are not written in the form of a squared norm. Since the third term describes the Kondo process, we treat it rigorously and have the following expression:  
 $-i \sum_{\mathbf{k}} V_{\mathbf{k}a}^* \langle \{c_{k\uparrow} \delta j_{a\downarrow}^{\mp}, \delta j_{a\downarrow}^{\pm} c_{a\uparrow}^{\dagger}\} \rangle = -i \sum_{\mathbf{k}} V_{\mathbf{k}a}^* \langle \{ \delta j_{a\downarrow}^{\mp} \delta j_{a\downarrow}^{\pm} c_{k\uparrow} c_{a\uparrow}^{\dagger} - \delta j_{a\downarrow}^{\pm} \delta j_{a\downarrow}^{\mp} c_{k\uparrow} c_{a\uparrow}^{\dagger} \} \rangle$   
 $= -i \sum_{\mathbf{k}} V_{\mathbf{k}a}^* \langle [\delta j_{a\downarrow}^{\mp}, \delta j_{a\downarrow}^{\pm}] c_{k\uparrow} c_{a\uparrow}^{\dagger} \rangle = -i \sum_{\mathbf{k}} V_{\mathbf{k}a}^* \langle [j_{a\downarrow}^{\mp}, j_{a\downarrow}^{\pm}] c_{k\uparrow} c_{a\uparrow}^{\dagger} \rangle.$

The second term of  $\langle \{i\mathbf{L}(c_{a\uparrow} \delta j_{a\downarrow}^{\mp}), \delta j_{a\downarrow}^{\pm} c_{a\uparrow}^{\dagger}\} \rangle$ , i.e.,  $\langle \{c_{a\uparrow} i[H, j_{a\downarrow}^{\mp}], \delta j_{a\downarrow}^{\pm} c_{a\uparrow}^{\dagger}\} \rangle$ , is rather complicate because it contains the commutator  $[H, j_{a\downarrow}^{\mp}]$ . This commutator is expanded as  $i[H, j_{a\downarrow}^{\mp}] = \pm \epsilon_a j_{a\downarrow}^{\pm} \mp (i) \sum_k \epsilon_k (V_{ka} c_{k\downarrow}^{\dagger} c_{a\downarrow} \pm V_{ka}^* c_{a\downarrow}^{\dagger} c_{k\downarrow}) \pm U n_{a\uparrow} j_{a\downarrow}^{\pm} \pm (i) \sum_{k,\ell}' (V_{ka} V_{\ell a} c_{k\downarrow}^{\dagger} c_{\ell\downarrow} \pm V_{ka}^* V_{\ell a}^* c_{\ell\downarrow}^{\dagger} c_{k\downarrow})$ , where (i) is applied only to the lower signs and the prime in sum denotes  $k \neq \ell$ . The first two are cancelled if we assume  $\epsilon_a \approx \epsilon_k$ , and the  $U$ -term can be neglected in the Kondo regime. The last term describes the round trip of a down-spin electron between the adatom and the substrate (tip), which is equivalent to  $(j_{a\downarrow}^{\pm})^2$ . Since we consider only single trip of a down-spin electron in this work, we neglect the term involving  $[H, j_{a\downarrow}^{\mp}]$ . Thus, the matrix element  $\mathbf{M}_a^{21/12}$  is given by  $\frac{-\langle i\mathbf{L}(c_{a\uparrow} \delta j_{a\downarrow}^{\mp}), \delta j_{a\downarrow}^{\pm} c_{a\uparrow}^{\dagger} \rangle}{\sqrt{\langle (\delta j_{a\downarrow}^{\mp})^2 \rangle} \sqrt{\langle (\delta j_{a\downarrow}^{\pm})^2 \rangle}} = \frac{i \sum_{\mathbf{k}} V_{\mathbf{k}a}^* \langle c_{k\uparrow} c_{a\uparrow}^{\dagger} [j_{a\downarrow}^{\mp}, j_{a\downarrow}^{\pm}] \rangle}{\sqrt{\langle (\delta j_{a\downarrow}^{\mp})^2 \rangle} \sqrt{\langle (\delta j_{a\downarrow}^{\pm})^2 \rangle}} \equiv \pm \gamma$  for the single-reservoir Anderson model. For the two-reservoir Anderson model, similar calculation gives rise to

$$\gamma_{ss(tt)} = \frac{i \sum_{\mathbf{k}} V_{\mathbf{k}a}^* \langle c_{k\uparrow}^s c_{a\uparrow}^{\dagger} + c_{k\uparrow}^t c_{a\uparrow}^{\dagger} [j_{a\downarrow}^{-s(t)}, j_{a\downarrow}^{+s(t)}] \rangle}{\langle (\delta j_{a\downarrow}^{-s(t)})^2 \rangle^{1/2} \langle (\delta j_{a\downarrow}^{+s(t)})^2 \rangle^{1/2}}.$$

## Appendix B: $\beta_{mn}$

We obtain the expressions of  $\beta_{mn}$  in terms of the definitions and the expressions of  $\xi_a^{\mp}$  given in Appendix A. The coefficients  $\beta_{mn}$  in front of the self-energy function, i.e.,  $i\Sigma_{mn}(\omega) = \beta_{mn}(i\Sigma_0^s(\omega) + i\Sigma_0^t(\omega))$ , are symmetric in exchanging their indices. We have obtained an expression  $1/\tau = i\langle (1 - 2n_{a\uparrow})[n_{a\downarrow}, j_{a\downarrow}^{\mp}] \rangle \langle (\delta j_{a\downarrow}^{\mp})^2 \rangle^{-1/2}$  in Appendix A. By using the operator identity  $[n_{a\downarrow}, j_{a\downarrow}^{\mp}] = \mp i j_{a\downarrow}^{\pm}$ , one can obtain a different expression for  $\tau$ , i.e.,

$$1/\tau = [\pm \langle j_{a\downarrow}^{\pm s, t} \rangle \mp 2 \langle j_{a\downarrow}^{\pm s, t} n_{a\uparrow} \rangle] / \sqrt{\langle (\delta j_{a\downarrow}^{\mp s, t})^2 \rangle},$$

which will be used in the expressions of  $\text{Re}[\beta_{mn}]$ . The final forms of  $\text{Re}[\beta_{mn}]$  are given by using  $\langle (\delta n_{a\downarrow})^2 \rangle \approx 1/4$  and  $\tau = 2$ . Since  $\langle j_{a\downarrow}^{+s(t)} \rangle < 0$  and  $\langle j_{a\downarrow}^{-s(t)} \rangle > 0$ , an inequality,  $\text{Re}[\beta_{12}] < \text{Re}[\beta_{11}] < \text{Re}[\beta_{22}]$ , is applied to the substrate side in which Kondo coupling exists. As for  $\text{Im}[\beta_{mn}]$ , we neglect all of them because  $\text{Im}[\beta_{mn}]$  contain the difference of relative fluctuations, which we assume they are the same.

We obtain the expressions of  $\beta_{mn}$  in terms of  $\xi_i^{\mp}$  given in Appendix A as follows:

### Real parts of $\beta_{mn}$ :

$$\begin{aligned} \text{Re}[\beta_{11}] &= \text{Re}[\xi_s^* \xi_s^-] = \left[ (\langle j_{a\downarrow}^{+s} \rangle - 2\langle n_{a\uparrow} j_{a\downarrow}^{+s} \rangle)^2 + (1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{-s} \rangle^2 \right] \frac{[4\langle (\delta n_{a\downarrow})^2 \rangle]^{-1}}{\langle (\delta j_{a\downarrow}^{-s})^2 \rangle} \\ &= \left[ \frac{1}{\tau^2} + \frac{(1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{-s} \rangle^2}{\langle (\delta j_{a\downarrow}^{-s})^2 \rangle} \right] \frac{1}{4\langle (\delta n_{a\downarrow})^2 \rangle} \approx \left[ \frac{1}{4} + \frac{(1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{-s} \rangle^2}{\langle (\delta j_{a\downarrow}^{-s})^2 \rangle} \right]. \end{aligned}$$

Only the index  $s$  changes to  $t$  for  $\text{Re}[\beta_{55}]$ .

$$\begin{aligned} \text{Re}[\beta_{22}] &= \text{Re}[\xi_s^* \xi_s^+] = \left[ (\langle j_{a\downarrow}^{-s} \rangle - 2\langle n_{a\uparrow} j_{a\downarrow}^{-s} \rangle)^2 + (1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{+s} \rangle^2 \right] \frac{[4\langle (\delta n_{a\downarrow})^2 \rangle]^{-1}}{\langle (\delta j_{a\downarrow}^{+s})^2 \rangle} \\ &= \left[ \frac{1}{\tau^2} + \frac{(1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{+s} \rangle^2}{\langle (\delta j_{a\downarrow}^{+s})^2 \rangle} \right] \frac{1}{4\langle (\delta n_{a\downarrow})^2 \rangle} \approx \left[ \frac{1}{4} + \frac{(1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{+s} \rangle^2}{\langle (\delta j_{a\downarrow}^{+s})^2 \rangle} \right]. \end{aligned}$$

Here, again, the index  $s$  changes to  $t$  for  $\text{Re}[\beta_{44}]$ .

$$\begin{aligned} \text{Re}[\beta_{12}] &= \text{Re}[\xi_s^* \xi_s^+] = \text{Re}[\beta_{21}] \\ &= \left[ (\langle j_{a\downarrow}^{+s} \rangle - 2\langle n_{a\uparrow} j_{a\downarrow}^{+s} \rangle)(-\langle j_{a\downarrow}^{-s} \rangle + 2\langle n_{a\uparrow} j_{a\downarrow}^{-s} \rangle) + (1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{-s} \rangle \langle j_{a\downarrow}^{+s} \rangle \right] \frac{[4\langle (\delta n_{a\downarrow})^2 \rangle]^{-1}}{\sqrt{\langle (\delta j_{a\downarrow}^{-s})^2 \rangle} \sqrt{\langle (\delta j_{a\downarrow}^{+s})^2 \rangle}} \\ &= \left[ \frac{1}{\tau^2} + \frac{(1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{-s} \rangle \langle j_{a\downarrow}^{+s} \rangle}{\sqrt{\langle (\delta j_{a\downarrow}^{-s})^2 \rangle} \sqrt{\langle (\delta j_{a\downarrow}^{+s})^2 \rangle}} \right] \frac{1}{4\langle (\delta n_{a\downarrow})^2 \rangle} \approx \left[ \frac{1}{4} + \frac{(1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{-s} \rangle \langle j_{a\downarrow}^{+s} \rangle}{\sqrt{\langle (\delta j_{a\downarrow}^{-s})^2 \rangle} \sqrt{\langle (\delta j_{a\downarrow}^{+s})^2 \rangle}} \right], \end{aligned}$$

$$\begin{aligned} \text{Re}[\beta_{14}] &= \text{Re}[\xi_s^* \xi_t^+] = \text{Re}[\beta_{41}] \\ &= \left[ (\langle j_{a\downarrow}^{+s} \rangle - 2\langle n_{a\uparrow} j_{a\downarrow}^{+s} \rangle)(-\langle j_{a\downarrow}^{-t} \rangle + 2\langle n_{a\uparrow} j_{a\downarrow}^{-t} \rangle) + (1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{-s} \rangle \langle j_{a\downarrow}^{+t} \rangle \right] \frac{[4\langle (\delta n_{a\downarrow})^2 \rangle]^{-1}}{\sqrt{\langle (\delta j_{a\downarrow}^{-s})^2 \rangle} \sqrt{\langle (\delta j_{a\downarrow}^{+t})^2 \rangle}} \\ &= \left[ \frac{1}{\tau^2} + \frac{(1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{-s} \rangle \langle j_{a\downarrow}^{+t} \rangle}{\sqrt{\langle (\delta j_{a\downarrow}^{-s})^2 \rangle} \sqrt{\langle (\delta j_{a\downarrow}^{+t})^2 \rangle}} \right] \frac{1}{4\langle (\delta n_{a\downarrow})^2 \rangle} \approx \left[ \frac{1}{4} + \frac{(1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{-s} \rangle \langle j_{a\downarrow}^{+t} \rangle}{\sqrt{\langle (\delta j_{a\downarrow}^{-s})^2 \rangle} \sqrt{\langle (\delta j_{a\downarrow}^{+t})^2 \rangle}} \right], \end{aligned}$$

$$\begin{aligned} \text{Re}[\beta_{15}] &= \text{Re}[\xi_s^* \xi_t^-] = \text{Re}[\beta_{51}] \\ &= \left[ (\langle j_{a\downarrow}^{+s} \rangle - 2\langle n_{a\uparrow} j_{a\downarrow}^{+s} \rangle)(\langle j_{a\downarrow}^{+t} \rangle - 2\langle n_{a\uparrow} j_{a\downarrow}^{+t} \rangle) + (1 - 2\langle n_{a\downarrow} \rangle)^2 \langle j_{a\downarrow}^{-s} \rangle \langle j_{a\downarrow}^{-t} \rangle \right] \frac{[4\langle (\delta n_{a\downarrow})^2 \rangle]^{-1}}{\sqrt{\langle (\delta j_{a\downarrow}^{-s})^2 \rangle} \sqrt{\langle (\delta j_{a\downarrow}^{-t})^2 \rangle}} \end{aligned}$$

